

A Review on Microwave Processing Technique in the Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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ABSTRACT

Microwave heating has a high potential technique to be used as an effective substitute for traditional furnace heating techniques in today's ceramic industries, including the synthesis of promising very high dielectric materials with relative permittivity, $\epsilon_r = 10^5$ of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). The microwave processing approach employs microwave radiation to heat materials more efficiently and uniformly to promote uniform densification. Hence, this approach improved the material's characteristics tremendously compared to the traditional furnace. As microwave heating lowers the reaction times, it has the potential to save both money and energy compared to conventional heating techniques. In CCTO processing, microwave energy was commonly used to replace the heating technique in the calcination stage, sintering stage, or both. This review delves into the historical development and advancements in microwave processing methods within ceramic manufacturing, particularly focusing on CCTO electroceramics. The aim is to assess the viability of microwave processing as a complete substitute for conventional furnace heating techniques in the production of CCTO.

Keywords: Microwave processing; CCTO; sintering; heating method; dielectric materials

1. Introduction

1.1 Background of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)

Bochu et al. [1] synthesized CCTO for the first time in 1979, and 21 years later, Ramirez et al. [2] and Subramanian et al. [3] discovered a high dielectric constant of 100,000 of the CCTO. Sonia and Kumar [4] found that CCTO has a high dielectric constant at ambient temperature and is almost constant throughout a broad frequency range of 1 Hz to 1 MHz. In CCTO, the crystal structure is built in the ratio of 1:3 A-site of pseudo-cubic perovskite ($\text{A}'\text{A}''\text{B}_4\text{O}_{12}$) [5]. Both calcium (Ca^{2+}) ions and copper (Cu^{2+}) ions occupy the larger sites of the crystal lattice, but the titanium (Ti^{4+}) cations obstruct at the B-site. With the A'' of Cu cations taking on a square-planar shape and the TiO_6 octahedra significantly tilted, the structure forms double simple perovskite cell. The significant cation size mismatch and the nature of the A'-site Ca^{2+} and A''-site Cu^{2+} cations caused the tilting of the octahedral coordination. The octahedral and square-planar structures occupy three-quarters of the A sites, with the remaining quarter being filled by

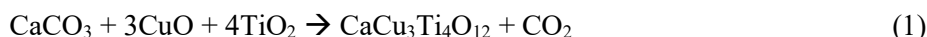
the large Ca ions. Despite exhibiting a Debye-like relaxation and rapidly decreasing to under 100 below 100 K, CCTO maintains its structural stability despite significant temperature shifts [6]. Some of the factors that researchers claim to give CCTO its distinct dielectric behaviors are the grain boundaries, twin boundaries, various planar defects, and the Ti ion displacement [7]. Due to these unique properties, CCTO can achieve 100,000 dielectric constant in a wide frequency range (1 Hz to 1 MHz) and wide working temperature (-173.15 °C to 326.85 °C) [8].

The unique behavior of this perovskite family has attracted a lot of microelectronic industries to miniaturize current devices or components. To date, CCTO has been widely applied as a dielectric capacitor, multilayer ceramic capacitor (MLLC), supercapacitor, piezoelectric devices, thermistors, electromagnetic interference (EMI) shielding, radio frequency components, piezoelectric energy harvesting, medical imaging and many other devices that require miniaturization with high capacitance.

1.2 Importance of Synthesis Methods

The CCTO production is a complex process involving multiple routes. CCTO is mostly synthesized by a conventional method of solid-state reaction, which is also known as conventional dry routes. Other conventional routes include wet chemistry, sol-gel, combustion synthesis, sonochemical-assisted process, and co-precipitation method [9–11]. In addition, modern state-of-the-art methods have also emerged in newer studies, such as microwave synthesis, molten salt, and microwave flash combustion [12]. Every method carries certain advantages and disadvantages that could be considered according to the desired product forms. The product of CCTO could be in the form of powder, pellets, dense ceramic, thin/thick film, nanomaterials, composite forms, and flexible forms [13–18].

Conventional synthesis of CCTO typically uses a solid-state reaction method for pellet-form products. This electrochemical uses precursors of calcium carbonate (CaCO₃), copper oxide (CuO), and titanium dioxide (TiO₂), and the chemical reaction is defined by the decomposition of the Eq. 1.



The technique involves mixing the three precursors, and then the milling process is used to make the mixed powder uniform and homogeneous before proceeding with the next step. The mixed powder was then calcined in a traditional furnace, and the temperature should be over 900 °C to achieve single-phase CCTO powder. The raw materials were proven to be fully transformed into a CCTO single phase in the shortest calcination duration, which is 6 hours [19]. After calcination, the powder was pressed into pellets of the desired size and proceeded to sinter to solidify the green body. The sintering process was traditionally fired using a furnace with a temperature setting of not exceeding 1040°C [20]. A typical solid-state reaction synthesis method for CCTO was simplified as Fig. 1 below. The total time taken by only mixing and milling, calcination, and sintering in the conventional solid-state reaction method roughly took around 46 hours, not including the time for preparation, weighing, and heating and cooling rate that could add several more days to the production time. Apart from time-consuming, a high amount of energy was also used to maintain the heating process at high temperatures of calcination and sintering. Nevertheless, this method delivers consistent results for the single-phase formation of CCTO at the end of the process.

Conventional synthesis techniques often require a long processing time as heat is transferred from the outer surface of the material to the interior, resulting in slow heat diffusion and long reaction times [12]. The impact increases energy consumption and reduces productivity in the industrial sector. When it comes to time-sensitive applications or large-scale production, this issue is especially detrimental. Traditional methods also require high temperatures to complete the synthesis of CCTO, which leads to significant energy usage to maintain high temperatures for long hours or even days. In addition, conventional heating methods like furnaces or kilns typically apply heat externally to diffuse into the material, resulting in non-uniform heating when the outer layers heat up much faster than the inner layers [12]. This uniformity is critical in material processing to avoid incomplete reactions, phase segregation, and the formation of secondary phases. For instance, titanium dioxide (TiO₂), copper oxide (CuO), or calcium titanate (CaTiO₃) may occur as byproducts [12]. These impurities or secondary phases might weaken the dielectric constant and insulating qualities of CCTO, which are essential for its usage in capacitors and other electronic devices. The limitation of heat transfer in conventional synthesis methods also often results in inhomogeneity of the final product, such as large grain size variations, phase segregation, and porosity. Several research have proven that the dielectric properties of CCTO are

significantly impacted by the processing stages of mixing [21], calcination [22,23], shaping [24], and sintering [25,26]. The CCTO qualities depend on the different parameter variations employed in each processing step, as the electrochemical properties are susceptible to the manufacturing process. Microwave processing can overcome these limitations by providing rapid and volumetric heating, which ensures uniform temperature distribution throughout the material. This leads to faster reaction times, reduced energy consumption, and improved homogeneity of the final product.

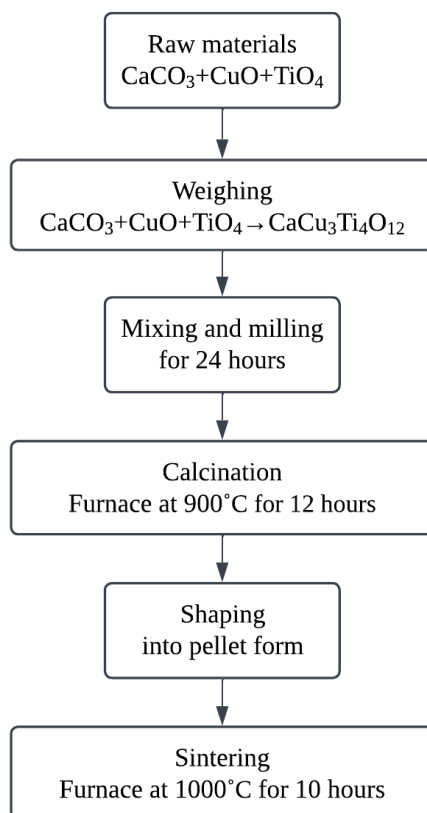


Fig. 1: The traditional solid-state reaction workflow

1.3 Overview of Microwave Processing

Microwave technology was first discovered in the early 20th century when the foundation emerged from electromagnetic wave theory, which included radio waves. The radio wave theory was then developed into radar technology that operated at microwave wavelength, which was widely used for detecting enemy locations during World War II. In 1945, an engineer working on radar technology accidentally initiated the creation of the microwave oven when he realized the microwave radiation from the radar had melted chocolate in his pocket; subsequently, the first commercial microwave oven, Radarange, was produced in 1947 for the food industry, although it was big and costly. Since then, microwave technology has gradually evolved into a common kitchen appliance mainly used for heating food worldwide. To date, while microwave ovens for food vary interestingly with many added functions, microwave technology has also expanded into other areas such as telecommunications [27], medical utilization, and material processing.

Microwave heating offers several key advantages over traditional synthesis methods for CCTO, especially in the heat transfer mechanism of the material. Microwave heating gives faster synthesis and processing time than conventional methods. This is because microwaves heat the material directly at the molecular level, where the reactions proceed more quickly. Compared to the conventional synthesis methods using furnace heating, the material is heated externally, and the heat must conduct into the bulk of the material, which leads to slower reactions and can be time-

consuming. Besides, microwave heating is generally more energy efficient since microwaves heat the material directly, so the energy is absorbed by the material with minimal energy loss compared to traditional heating. In traditional heating, much of the energy is lost to the surrounding environment or heating element as heat needs to be transferred through a medium before reaching the material. Microwaves can also heat specific materials more effectively depending on their dielectric properties, allowing for selective heating for certain parts of an object or material. So, it gives precision in controlling heat distribution to improve product quality and reduce waste in industrial processes. Microwaves provide a non-contact heating method, without using heating elements, to reduce the wear and tear on equipment and avoid contamination. Besides, the ability to heat materials quickly means that processes can be accelerated and give faster product turnaround.

In certain material processing such as sintering, calcination, or curing, microwave heating has been shown to improve material properties, such as more uniform microstructure, better bonding, and enhanced crystallization, hence improving the properties of the final product to lead to better performance and durability of the product material. Numerous industrial and scientific application uses microwave-assisted heating for material synthesis to suit their respective benefits, including nanoparticle production, increased reaction rate, energy conservation, extremely quick heating, decreased processing temperature and time, fine-tuning microstructure, and better material properties and performance, particularly dielectric properties [27,28].

The review focuses on the fundamentals of microwave heating and its possibility of replacing conventional heating in material processing, particularly in CCTO electroceramics. The scope is to understand the principle of microwave heating on CCTO and to review the development of microwave utility in CCTO syntheses, such as the solid-state reaction method, sol-gel method, and the newly emerging methods, which are hydrothermal synthesis and combustion synthesis. The objective of this review is to determine if microwave processing can completely replace conventional furnace heating techniques in CCTO production.

2. Fundamentals of Microwave Processing

3.1 Principles of Microwave Heating

Microwave heating differs from the ordinary heating process. Theoretically, in conventional heating, heat is transferred from one material or system to another due to temperature differences that occur through three main ways, which are conduction, convection, and radiation. Microwave heating uses energy conversion instead of heat transfer. The magnetron, the most crucial component of a microwave source, is used to make this energy conversion. A magnetron transforms low-frequency electrical grid energy into high-frequency electromagnetic energy. The frequency of the produced electromagnetic radiation is typically 2.45 GHz for microwave heating applications [29]. This frequency complies with the termed industrial, scientific, and medical (ISM) frequencies, and it is commonly fabricated for commercial use, particularly in commercial microwave ovens for households [30]. Microwave heating does not depend on physical contact or fluid movement; thus, it could provide more uniform heating of materials. It transfers heat directly into the materials and allows direct heating on the material itself without needing to heat the surrounding environment. Hence, it reduces heat loss by saving the unnecessary energy and time required to reach the desired temperature. Microwave radiation also emanates into the medium of materials, triggering the vibration of their polar molecules, resulting in rapid heating from the inside of the medium instead of the surface. This differs from traditional fire heating, where heat travels from the surface inward, which could result in uneven heating on the inside of the material. The power absorbed by the microwave was calculated based on Maxwell's equation, where the absorbed microwave power is proportional to the electric field distribution on the material as in Eq. 2,

$$P = \sigma |E|^2 = 2\pi f \epsilon_0 \epsilon_r \tan \delta |E|^2 \quad (2)$$

where power absorbed per unit volume, P (W m^{-3}), E is the magnitude of the internal field (Vm^{-1}), σ is the total effective conductivity (Sm^{-1}), f is the frequency (2.45 GHz), ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.86 \times 10^{-12} \text{ Fm}^{-1}$), ϵ_r is the relative dielectric constant, and $\tan \delta$ is the loss tangent.

In the material processing area, microwave technology has received much attention from researchers worldwide to study its potential in ceramic processing. Ceramics are materials with low heat conductivity and are treated at high temperatures. Researchers have been seeking to use microwave volumetric heating to replace the traditional firing process in ceramic processing [31]. In the ceramic processing industry, electroceramics have a greater potential for usage in microwave heating applications due to their great dielectric properties. It is related to dielectric properties that are one of the mechanisms of heating for microwaves, where materials that possess higher dielectric constants generally convert microwave energy to heat with more efficiency. Not all ceramics are equally suitable for microwave heating. Careful selection based on dielectric characteristics is critical. This is because many room-temperature ceramics do not absorb microwaves extensively at 2.45 GHz, resulting in high attenuation distances. However, their absorption may be enhanced by raising the temperature by adding crucibles such as SiC, carbon, and binders, modifying their microstructure and defect structure by changing their form or tuning the frequency of the radiation [32].

The dielectric heating mechanism in microwaves happens when a material with polar molecules interacts with the oscillation of microwave radiation from the electric field. At high frequencies, the microwave field alternates to cause a force on the material's dipoles and rotate the particles inside the material. The rotation of the particles converts the microwave energy into thermal energy to effectively heat the material from the inner to the outer layers. This mechanism enables the materials to heat quickly and evenly, especially when the dielectric loss is considerable.

The penetration of microwave radiation into a material depends on its dielectric properties. Material with high dielectric properties absorbs microwave energy more efficiently, so the conversion of energy happens near the surface of the material. In contrast, materials with low dielectric constant have poor energy absorption, causing the microwave to penetrate deeper into the material for energy conversion to happen [33]. This could lead to uneven heating if the material has different variations of dielectric characteristics.

3.2 Advantages of Microwave Processing

The evolution of material processing has witnessed significant advancements with the incorporation of microwave technology. In the realm of CCTO production, the microwave approach presents a transformative alternative to traditional methods that consume lengthy heating processes and high energy consumption. This innovation harnesses the unique properties of microwave radiation, enabling rapid and uniform heating of materials. It promotes faster synthesis time, better control over the phase formation of CCTO, improving its structural and electrical properties, and reducing material waste. The unique principle of microwave heating significantly reduces processing times while improving phase purity and microstructural homogeneity. There was research on zinc (Zn) doped CCTO that utilizes microwave processing to achieve optimal conditions for sintering and densification, where the dielectric properties were enhanced due to improved crystallinity and reduced grain boundaries when subjected to rapid microwave heating [34].

Microwave processing of materials, particularly CCTO, also notably offers economic and environmental benefits that elevate its importance in modern manufacturing. As it reduces processing times significantly, this enhanced technique contributes to lower energy consumption, decreases operational costs, and minimizes the carbon footprint associated with the production process. Moreover, the rapid heating also engages in heightened material efficiency that leads to waste reduction and improves yields. The stable thermal control and surroundings during synthesis have enabled high-quality throughput with fewer impurities and complete phase formation.

3. Microwave Processing Techniques for CCTO Synthesis

3.1 Microwave Solid-State Reaction

The microwave-assisted solid-state reaction is an innovative method for CCTO synthesizing, where the heating process in this reaction is replaced with microwave heating. There are several methods to enhance heating, whether during calcination, sintering, or both. In 2007, powder-formed CCTO was successfully synthesized in a short amount of time and with comparatively low energy using a microwave technique [35]. The microwave technique utilized a commercial multimode microwave oven with the standard specification of 1600 watts at 2.45 GHz. The microwave was modified with a radiation thermometer and an automatic time controller to monitor the process. Inside the microwave,

the sample was put into an alumina crucible surrounded by SiC powder that has excellent properties to absorb microwave radiation and increase the sample temperature efficiently. The sample result turned single phase with a higher dielectric constant in only 2 hours compared to the sample synthesized conventionally using an electric furnace, which consumes 72 hours to yield similar results. Ramirez et al. [36] also used a commercial microwave oven that was modified into a furnace that contained SiC susceptor to aid with the absorption of microwave radiation. The experiment modified the stoichiometry ratio to produce a two-phase system of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$ (CCTO/CTO), which is considered intriguing for its great non-ohmic characteristics. However, its dielectric permittivity is lower than that of pure CCTO. In the experiment, the conventional calcined CCTO pellets were sintered for only 30 minutes at 1050°C in the microwave furnace to achieve higher non-ohmic behavior compared to conventional sintering.

In 2009, a microwave synthesis was conducted to produce CCTO using a 2.45 GHz and 800-watt microwave oven. The research used a double-layer crucible to optimize microwave absorption, where one of the crucibles was made of graphite. The microwave radiation was absorbed by graphite before transforming into heat, and the heat was applied to the sample powder to increase the heat to the desired sintering temperature. The result returned that a single-phase CCTO was successfully produced in only 15 minutes using microwave synthesis compared to a conventional solid-state reaction that took 12 hours of 900°C firing [24]. In 2012, a 2.45 GHz, 8.8 kWatt microwave furnace was built utilizing eight magnetrons to sustain a higher temperature setting. The conventionally calcined CCTO pellets were sintered in the microwave at varied temperatures for 15 minutes. The result shows that the dielectric constant increased with the increase of temperature. Microwave synthesis was able to deliver the same amount of dielectric constant as the conventional synthesis but with much lower time and energy consumption [37].

Moving forward to 2016, an innovative microwave furnace built by VB ceramics consultants, India was used to pre-sinter the calcined CCTO pellet for 30 minutes at 1080 °C. The result of densification was compared with conventionally sintered CCTO pellets, and it turns out that the product that underwent microwave pre-sintering had a denser structure of 97% relative density, which is 3% higher than the conventionally synthesized products [38]. The microwave furnace was also used in 2018, where the hybrid microwave synthesis managed to produce CCTO powder that is fine, monodisperse, and almost pure, with a size between 300 and 500 nm, before solidifying with conventional sintering. However, there is a heterogeneous grain size distribution on the product since there is non-uniform heat distribution during direct microwave heating [39].

Sulaiman et al. [40,41], in 2020, used a domestic microwave oven with 2.45 GHz and 1 kW specification to process the calcination of CCTO pellets. The microwave calcination process utilized an enhanced SiC-feldspar susceptor crucible to aid the microwave absorption and transform the energy into heat. The CCTO pellet sample was made sure to have direct contact with the susceptor crucible for optimum heat transfer from the material surface and dwell into the sample. When varying the calcination temperature from 500 °C to 900 °C in 1 hour, the pure phase CCTO formed at 600°C temperature [23]. Another study by them also varies calcination time from 1 hour to 9 hours, and based on the experiment, 7 hours of calcination duration produces the highest percentage of CCTO composition [41].

Various research in 2022 [43–45] have compared the ceramic sintering processing through conventional muffle furnaces and modified microwave furnaces (VB ceramics) for lanthanum-doped CCTO and later in 2023 for Gadolinium (Gd)-doped and Europium-doped CCTO. All the results from the research showed a successful single-phase XRD pattern for microwave heating despite the microstructure difference where the grain size changes based on each of the doping concentration effects. The microstructure results for all types of doped showed that CCTO has a finer grain size when processed with microwave sintering compared to the grain size for conventional sintering. For dielectric properties, the ionic radius of gadolinium, which lessens the segregation of the Cu-rich phase along the grain boundaries, was linked to the lower dielectric constant than pure CCTO in the room temperature dielectric response observed over the frequency range of 10 Hz to 20 MHz. Nevertheless, both conventional and microwave sintering samples produce great dielectric constants with stable low loss at high frequencies, which were 10^5 to 10^7 in ambient temperature. But notably, microwave heating gives out a very small dielectric loss and high dielectric constant at 10 Hz for Gd-doped. On top of the excellent conservation of sintering time and energy by taking only 30 minutes of 1100 °C heating using the microwave to achieve such results compared to conventional heating that took 12 hours for a similar operating temperature.

3.2 Microwave-Assisted Sol-Gel Synthesis

The fundamentals of the sol-gel method start with two powder precursors of calcium acetate and copper acetate being mixed with acetic acid and stirred at a hot temperature. Titanium isopropoxide is added later to the dissolved solution based on the stoichiometric ratio to form a clear CCTO solution. The solution was then proceeded with the drying process to turn into precipitation before it undergoes the standard calcination and sintering process. Shuhua et al. [42] have successfully fabricated a nano-ultrafine CCTO ceramic using sol-gel, and a fine homogeneous microstructure with stable electrical properties was produced after sintering at 1000°C for 2 hours. The sol-gel method also used nitrate and alkoxide precursors and successfully obtained a giant dielectric constant of more than 35,000 at 1 kHz [43]. The research claimed that the dielectric permittivity of CCTO synthesized using the sol-gel approach is at least three times greater than other low-temperature and solid-state reaction methods [44]. The sol-gel synthesis method is especially suitable to form the thin film shape of CCTO [45,46]. This method has produced a stable electrical property for the application of sensor and capacitor layers such as gas sensors, pyroelectric sensors, and multilayer capacitors [4,47,48].

Microwaves in sol-gel chemistry substitute the heating process to provide rapid and uniform heating that speeds up the synthesis of materials [49]. Microwave heating can replace the drying process, calcination, or sintering process in sol-gel synthesis. The microwave-assisted sol-gel method highlighted a higher dielectric constant, decreased dielectric loss, and a minimal temperature coefficient of capacitance. Most importantly, this enhanced method reduced the processing time and temperatures, which led to great energy efficiency and time management. In the sol-gel method, the sintering temperature and time duration are typically the same as in other techniques. The dielectric properties of the CCTO ceramics are significantly impacted by the long sintering time. Hence, the tailored dielectric constants and nonlinear coefficients can be produced by choosing an appropriate sintering time based on the application needs [50].

3.3 Microwave Hydrothermal Synthesis

Hydrothermal synthesis is a process that produces crystalline materials by performing chemical reactions in water at high temperatures and pressures, commonly in an autoclave or other enclosed vessel. At the designated high pressure in the autoclave, the water remains liquid due to the high pressure, which creates a perfect atmosphere to promote certain reactions in the material. An effort to embed nanostructural and giant dielectric properties of CCTO succeeded by utilizing a hydrothermal route to cover TiO₂ at the outer surface of CCTO [51]. The sealed autoclave that requires heating that typically ranges from 150 °C to 250 °C could use the unique feature of microwave heating that selectively heats from the inside of the autoclave without needing to heat the surroundings. The hydrothermal synthesis encourages the formation of CCTO nanoparticles or microcrystals with stable stoichiometry.

3.4 Microwave Combustion Synthesis

Microwave combustion has first synthesized a polycrystalline CCTO ceramic nanopowder ranging from 50 to 70 nm [12]. Microwave combustion is distinct from conventional synthesis routes as the reaction occurs at the molecular level, significantly reducing processing time. In this innovation, the dissolved solution is subjected to microwave irradiation in a mixture containing oxidizers and fuel. CCTO residual powder was calcined at 800°C and 900°C for 5 hours to eliminate the powder's waste products of CaTiO₃, TiO₂, and CuO. The improved dielectric properties were produced with a value approaching 20,000 with a dielectric loss of 0.51 at 100 Hz [52]. These cost-effective and fast response synthesis techniques have been further improved to overcome contamination and environmental issues.

4. Discussion

For CCTO processing, microwave technology has indeed produced better output than the conventional method based on all the research done to date. The ability to heat materials directly at the molecular level has not only saved the processing time and the usage of energy but also improved the product qualities, including dielectric properties and uniform microstructure. This precision reduces the waste of energy to improve the sustainability of material synthesis. While microwave heating shows excellent potential, it still has not completely replaced furnace heating in all

applications. Specialized equipment and process controls are required to optimize the heating dynamics of the microwaves for CCTO. For instance, a good susceptor and crucible are always included in all the research reviewed. It is safe to say that a good combination of susceptor or crucible determines the effectiveness of microwave heating for CCTO production. To date, much research still combines microwave heating with furnace heating. There is research that only uses microwaves for solidifying the CCTO product, and there is research that only uses microwaves for powder calcination. Microwave heating's effectiveness also depends on the dielectric properties of the material, where some ceramics may not heat uniformly, risking thermal shocks or uneven results due to hotspots. In the future, as microwave technology advances and its limitations are well addressed, it may gradually replace conventional furnace heating in various applications. Nevertheless, for CCTO materials with complex properties or specific requirements, such as multilayer CCTO or doped CCTO with unique material, furnace heating still plays a role in niche or complementary processes. The industries increasingly recognize the advantages of microwave processing technology for CCTO production. As the limitations are addressed, it is expected to gradually replace conventional furnace heating in a wider range of applications.

5. Conclusion

Since the discovery of microwave heating, the microwave processing technique has developed progressively from the early years to date in the desire to shorten the processing time and save the processing energy to push the miniaturization device industry to the limit. The promise of CCTO in microwave applications is demonstrated by its historical development, and the benefits of using microwave heating to synthesize this material are increasingly evident. Microwave heating might greatly improve the processing of CCTO by providing a quicker and less expensive substitute for conventional furnace firing, making it easier to incorporate into cutting-edge electronic products. As research develops, microwave heating in CCTO synthesis might lead to new uses and help promote environmentally friendly materials processing techniques. Not all ceramics are equally appropriate for microwave heating, so making careful selections based on dielectric characteristics is critical. To avoid problems such as thermal shock or uneven heating, the heating process must be monitored and controlled. Specialized microwave ovens or kilns may be required to meet ceramics' particular heating dynamics.

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References

- [1] Bochu B, Deschizeaux MN, Joubert JC, Collomb A, Chenavas J, Marezio M. Synthèse et caractérisation d'une série de titanates pérovskites isotypes de $[\text{CaCu}_3](\text{Mn}_4)\text{O}_{12}$. *J Solid State Chem*, 1979;29(3):291-298.
- [2] Ramirez AP, Subramanian MA, Gardel M, Blumberg G, Li D, Vogt T, Shapiro SM. Giant dielectric constant response in a copper-titanate. *Solid State Commun*, 2000;115(5):217-220.
- [3] Subramanian MA, Li D, Duan N, Reisner BA, Sleight AW. High Dielectric Constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ Phases. *J Solid State Chem*, 2000;151(2):323-325.
- [4] Sonia MC, Kumar P. Microwave assisted sol-gel synthesis of high dielectric constant CCTO and BFN ceramics for MLC applications. *Process Appl Ceram*, 2017;11(2):154-159.
- [5] Infantiya SG, Aslinjensipriya A, Reena RS, Deepapriya S, Rodney JD, Das SJ, Raj CJ. Calcium copper titanate a perovskite oxide structure: effect of fabrication techniques and doping on electrical properties—a review. *J Mater Sci Mater Electron*, 2022;33(22):15992-16028.
- [6] Zhang J, Wang D, Hao R, Guo X, Chen Z, Lei Z, Li Y, Li L. SrTiO_3 -modified $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics with low dielectric loss and excellent temperature stability for X8P capacitors. *J Mater Sci Mater Electron*, 2023;34(7):1148.
- [7] Hutagalung SD, Ibrahim MIM, Ahmad ZA. The role of tin oxide addition on the properties of microwave treated $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Mater Chem Phys*, 2008;112(1):83-87.

- [8] Abdelal OA, Hassan AA, Ali MES. Dielectric Properties of Calcium Copper Titanates ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) Synthesized by Solid State Reaction. *Int J Adv Res Chem Sci*, 2014;1(1):4-10.
- [9] Kumari N, Meena S, Rathore D, Singhal R, Dwivedi UK. Study of dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ synthesized via different routes: Effect of sintering temperature. *Ceram Int*, 2023;49(2):2549-2556.
- [10] Ahmadipour M, Ain MF, Ahmad ZA. A Short Review on Copper Calcium Titanate (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition, and Sensing Application. *Nanomicro Lett*, 2016;8(3):291-311.
- [11] Makhoul E, Boulos M, Cretin M, Lesage G, Miele P, Cornu D, Bechelany M. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Perovskite Materials for Advanced Oxidation Processes for Water Treatment. *Nanomater*, 2023;13(1).
- [12] Evangeline GT, Annamalai AR, Magdaline TB. Modern Synthesis and Sintering Techniques of Calcium Copper Titanium Oxide ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) Ceramics and Its Current Trend in Prospective Applications: A Mini-Review. *Nanomater*, 2022;12(1).
- [13] Sharifuddin SM, Nor MSM, Pabli FAM, Chueangchayaphan W, Ahmad Z A, Sulaiman M A. Modification of curing, morphological, mechanical and electrical properties of epoxidised natural rubber (ENR-25) through the addition of copper calcium titanium oxide (CCTO). *Polymer Bull*, 2022;79(1).
- [14] Thiruramanathan P, Karthikeyan N, Srinivasan R, Manjula S, Selvakumar K. Investigating the dielectric and ferroelectric properties of $(\text{Bi}_4\text{Ti}_3\text{O}_{12})_{0.4}-(\text{CaCu}_3\text{Ti}_4\text{O}_{12})_{0.6}$ nanocomposite ceramics, thin films and thick films for microwave and microelectronic applications. *J Alloys Compd*, 2024;994(1):174668.
- [15] Ramadan RM, Labeeb AM, Ward AA, Ibrahim AMH. New approach for synthesis of nano-sized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder by economic and innovative method. *J Mater Sci Mater Electron*, 2020;31(12):9065-9075.
- [16] Zu H, Wang C, He X, Wang B, Liu H, Huang H, Bian J, Cao G. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics with giant permittivity prepared by reduction-reoxidation method. *Ceram Int*, 2023;49(13):20870-20877.
- [17] Han J, Park SH, Jung YS, Cho YS. High-performance piezoelectric energy harvesting in amorphous perovskite thin films deposited directly on a plastic substrate. *Nat Commun*, 2024;15(1).
- [18] Jiang M, Cheng Z, Zhao D, Zhang L, Xu D. Preparation and characterization of Mg-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films. *Trans Nonferrous Met Soc China*, 2022;32(6):1589-1597.
- [19] Mohamed JJ, Noor MM, Hutagalung SD, Ahmad ZA. The Effects of Different Calcination Parameters on CCTO Formation, 2008.
- [20] Mohamed JJ, Hutagalung SD, Ahmad ZA. Influence of sintering parameters on melting CuO phase in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J King Saud Univ Eng Sci*, 2013;25(1):35-39.
- [21] Bender BA, Pan MJ. The effect of processing on the giant dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Mater Sci Eng B Solid State Mater Adv Technol*, 2005;117(4):339-347.
- [22] Karim SA, Sulaiman MA, Masri MN, Ahmad ZA, Ain MF. The dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at various calcination temperatures. *Mater Sci Forum*, 2017;888(1):117-120.
- [23] Mohd Pabli FA, Teo WN, Sharifuddin SM, Mat Nor MS, Wan Ali WFF, Ain MF, Juliewatt J, Sulaiman MA. Effect of Calcination Temperature to the Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using Enhanced Microwave Processing. *IOP Conf Ser Earth Environ Sci*, 2020.
- [24] Almeida AFL, Fachine PBA, Graça MPF, Valente MA, Sombra ASB. Structural and electrical study of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) obtained in a new ceramic procedure. *J Mater Sci Mater Electron*, 2009;20(2):163-170.
- [25] Löhnert R, Schmidt R, Töpfer J. Effect of Sintering Conditions on Microstructure and Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) Ceramics. *J Electroceram*, 2015;34(4):241-248.
- [26] Mao P, Wang J, Zhang L, Liu S, Zhao Y, Sun Q. Rapid fabrication and improved electrical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics by sol-gel and spark plasma sintering techniques. *J Mater Sci Mater Electron*, 2019;30(24):13401-13411.
- [27] Hutagalung SD, Ibrahim MIM, Ahmad ZA. Microwave assisted sintering of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Ceram Int*, 2008;34(4):939-942.
- [28] Mondal A, Shukla A, Upadhyaya A, Agrawal D. Effect of porosity and particle size on microwave heating of copper. *Sci Sinter*, 2010;42(2):169-182.
- [29] Palma V, Barba D, Cortese M, Martino M, Renda S, Meloni E. Microwaves and heterogeneous catalysis: A review on selected catalytic processes. *Catalysts*, 2020;10(3).
- [30] Liu M. *Sintering Technology*. IntechOpen, Rijeka, 2018.

- [31] Thostenson ET, Chou TW. Microwave processing: fundamentals and applications. *Compos Part A Appl Sci Manuf*, 1999;30(8):1055-1071.
- [32] Menezes RR, Souto PM, Kiminami RHGA. *Microwave Fast Sintering of Ceramic Materials*, 2012. www.intechopen.com.
- [33] Horikoshi S, Catalá-Civera JM, Schiffmann RF, Fukushima J, Mitani T, Serpone N. Materials Processing by Microwave Heating. *Microwave Chem Mater Process*, 2024;389-468.
- [34] Sulaiman MA, Sharifuddin SM, Anadin N, Mohd Pabli FA, Mohamed JJ, Ibrahim N, Ali A, Masri MN. Zn-Doped Calcium Copper Titanate Synthesis via Microwave-Assisted Technique. *Malays J Bioeng Technol*, 2024;1(1):13-19.
- [35] Yu H, Liu H, Luo D, Cao M. Microwave synthesis of high dielectric constant $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Mater Process Technol*, 2008;208(1):145-148.
- [36] Ramírez MA, Bueno PR, Longo E, Varela JA. Conventional and microwave sintering of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{CaTiO}_3$ ceramic composites: Non-ohmic and dielectric properties. *J Phys D Appl Phys*, 2008;41(11).
- [37] Kumar R, Zulfequar M, Singh VN, Tawale JS, Senguttuvan TD. Microwave sintering of dielectric $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: An interfacial conductance and dipole relaxation effect. *J Alloys Compd*, 2012;541(1):428-432.
- [38] Rani S, Ahlawat N, Punia R, Kundu RS, Ahlawat N. Effect of microwave-assisted sintering on dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic. *AIP Conf Proc*, 2016;1731(1).
- [39] Riquet G, Marinel S, Breard Y, Harnois C, Pautrat A. Direct and hybrid microwave solid state synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic: Microstructures and dielectric properties. *Ceram Int*, 2018;44(15):15228-15235.
- [40] Sharifuddin SM, Sulaiman MA, Mohamed JJ, Pabli AFM, Chueangchayaphan W. Influence of Vulcanization System on the Mechanical Properties of CCTO/ENR50 Composite. *IOP Conf Ser Earth Environ Sci*, 2020.
- [41] Na TW, Pabli FAM, Sharifuddin SM, Nor MSM, Wan Ali WFF, Sulaiman MA. Effect of calcination time on the microstructure and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using enhanced microwave processing. *Malays J Microsc*, 2020;16(1).
- [42] Jin S, Xia H, Zhang Y, Guo J, Xu J. Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic via a sol-gel method. *Mater Lett*, 2007;61(6):1404-1407.
- [43] Liu L, Fan H, Fang P, Jin L. Electrical heterogeneity in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics fabricated by sol-gel method. *Solid State Commun*, 2007;142(11):573-576.
- [44] Liu L, Fan H, Fang P, Chen X. Sol-gel derived $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics: Synthesis, characterization and electrical properties. *Mater Res Bull*, 2008;43(7):1800-1807.
- [45] Mishra AK, Dwibedy D, Devi M, Panigrahi MR. Giant Dielectric Behaviour of Nb Modified CCTO Thin Film Prepared by Modified Sol-Gel Route. *Trans Electr Electron Mater*, 2020;21(2):315-323.
- [46] Bretos I, Jiménez R, Ricote J, Rivas AY, Echániz-Cintora M, Sirera R, Calzada ML. Low-temperature sol-gel methods for the integration of crystalline metal oxide thin films in flexible electronics. *J Solgel Sci Technol*, 2023;107(2):269-277.
- [47] Li Z, Fan H. Structure and electric properties of sol-gel derived $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics as a pyroelectric sensor. *Solid State Ion*, 2011;192(1):682-687.
- [48] Parra R, Savu R, Ramajo LA, Ponce MA, Varela JA, Castro MS, Bueno PR, Joanni E. Sol-gel synthesis of mesoporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films and their gas sensing response. *J Solid State Chem*, 2010;183(5):1209-1214.
- [49] Predoană L, Karajz A, Odhiambo VO, Stanciu I, Szilágyi I M, Pokol G, Zaharescu M. Influence of the Microwaves on the Sol-Gel Syntheses and on the Properties of the Resulting Oxide Nanostructures. www.intechopen.com.
- [50] Sun DL, Wu AY, Yin ST. Structure, properties, and impedance spectroscopy of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by sol-gel process. *J Am Ceram Soc*, 2008;91(2):169-173.
- [51] Zhao J, Chen M, Tan Q. Embedding nanostructure and colossal permittivity of TiO_2 -covered CCTO perovskite materials by a hydrothermal route. *J Alloys Compd*, 2021;885(1):160948.
- [52] Kumar R, Zulfequar M, Sharma L, Singh V N, Senguttuvan TD. Growth of Nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramic by the Microwave Flash Combustion Method: Structural and Impedance Spectroscopic Studies. *Cryst Growth Des*, 2015;15(6):150206133850007.